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## (54) Process for producing a high carotene content oil.

(57) A process for producing a high carotene content oil comprises blowing steam through an oil containing carotene in an amount of at least 500 ppm under a reduced pressure of not higher than 10 torr whilst maintaining the temperature at 110 to 150°C. A process for producing a concentrated carotene oil which is useful for the above process comprises dissolving crude palm oil in an organic solvent at a concentration of 5 to 30% by weight, cooling the resulting solution at a cooling rate of, at the highest, 1°C/min. to precipitate a crystalline part of the oil and recovering a non-crystalline part.

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The present invention relates to a process for producing a high carotene content oil. More specifically, it relates to a process for producing a high carotene content oil which is cheap and has a palatable flavor.

Carotenes are carotenoid hydrocarbons and there are α-, β- and γ-isomers. They have been known as provitamin A.

Recently, in addition to provitamin A, they have been noted with respect to prevention of cancers in view of their biological antioxidant activity, free radical scavenger activity and singlet oxygen eliminator activity. Also, many drinks characterized by containing carotenes and carotene preparations have been marketed.

Carotenes used in these products are produced by a synthetic method starting from β-ionone or by concentration of, or extraction from natural products such as carrot and palm oil. In particular, in view of the recent tendency of increase in preference for natural products, natural carotenes are chosen and carrot carotenes and palm carotenes have been much more noted.

As a concentration method of natural carotenes, JP-A 2-40358 discloses a process for producing a carotene concentrated oil, wherein unrefined palm oil is subjected to interesterification, following by further addition of unrefined palm oil and removal of esters by distillation. However, this carotene concentrated oil has a significant odor and is not suitable for use in foods.

As an extraction method of natural carotenes, JP-A 64-38061 discloses a method wherein a carotene containing oil is subjected to alcoholysis, followed by extraction and isolation with a hydrophilic organic solvent and water. JP-A 62-241970 discloses the separation of carotenes by silica gel chromatography with a mixed solvent of acetone and hexane. However, chromatography is expensive and the carotene product obtained such a method still has a bad flavor and is not suitable for foods.

Thus, a method for concentration or extraction of carotenes having a good flavor which is cheap and suitable for foods has not been known heretofore in the prior art. This is an obstacle to the popularization of carotene containing foods.

Under these circumstances, the present inventors have intensively looked for methods for the concentration or extraction of carotene which are cheap and can provide carotene having a palatable flavor. As a result, it has been found that a high carotene content oil having a palatable flavor can be obtained by adding a commercially available carotene preparation to an oil and deodorizing with steam under specific temperature conditions. Furthermore, the present inventors have found a novel process for producing a carotene concentrated oil which can be fed to the above deodorizing step by subjecting crude palm oil to solvent fractionation under specific conditions and recovering a non-crystalline part. Thus, the present invention was discovered.

The main object of the present invention is to provide a process for producing a high carotene content oil which is cheap and can provide a carotene oil having a palatable flavor.

This object as well as other objects and advantages of the present invention will become apparent to a person skilled in the art from the following description.

According to the present invention there is provided a process for producing a high carotene content oil which comprises blowing steam through an oil containing carotene in an amount of at least 500 ppm under a reduced pressure of not higher than 10 Torr whilst maintaining the temperature at 110 to 150°C.

The present invention also provides a process for producing a carotene concentrated oil which comprises dissolving crude palm oil in an organic solvent at a concentration of 5 to 30% by weight, cooling the resulting solution at a cooling rate of, at the highest, 1°C/min. to precipitate a crystalline part of the oil and recovering a non-crystalline part.

In the present invention, "carotene" includes α-, β- and γ-isomers and mixtures thereof.

## Production of high carotene content oil

The oil containing carotene in an amount of at least 500 ppm to be used in the present invention can be obtained by, if necessary, adding a carotene containing material such as a commercially available carotene preparation to an edible oil. The edible oil is not specifically limited and any oil produced by known oil refining steps such as degumming, deacidification and bleaching can be used. In addition, a carotene concentrated oil as described hereinafter can be used. When the carotene concentrated oil is used, there is no need to add a carotene containing material and therefore an economic process can be achieved. The carotene concentrated oil is preferably subjected to deacidification and bleaching according to a conventional method.

In the process of the present invention, steam is blown through the oil under specific temperature and pressure conditions to deodorize the oil.

The deodorizing temperature is 110 to 150°C, preferably 135 to 145°C. When the deodorizing temperature is lower than 110°C the resulting concentrated oil has a bad flavor and when the temperature is higher than 150°C decomposition of carotene takes place and recovery of carotene is reduced.

The deodorizing pressure is a reduced pressure of 10 Torr or lower, preferably, 5 Torr or lower. When the

pressure exceeds 10 Torr decomposition of carotene and even oxidization of the oil takes place and the resulting concentrated oil has a bad flavor.

The amount of steam to be blown through and the deodorizing time are not specifically limited. Normally, when 3.3% by weight of steam based on the oil per hour is blown through, the deodorizing time is 30 to 200 minutes, preferably 70 to 180 minutes. When the deodorizing time is shorter than 30 minutes the desired deodorization cannot be expected. On the other hand, when the deodorizing time exceeds 200 minutes no improvement of deodorization effect is obtained and decomposition of carotene even takes place.

Any steam deodorizer can be used. Examples thereof include a Girdler semi continuous deodorizer.

The high carotene content oil thus obtained normally contains carotene in an amount of at least 500 ppm, preferably 1,000 ppm to 30,000 ppm and has a palatable flavor. It can be used for the production of foods such as drinks, ice cream, stuffings and margarine without deterioration of food flavor. In addition, the oil can be used as it is or encapsulated as health foods.

Production of carotene concentrated oil

The carotene concentrated oil of the present invention is produced by dissolving crude palm oil in an organic solvent at a concentration of 5 to 30% by weight, cooling the resulting solution at a cooling rate of 1°C or less per minute to precipitate a crystalline part of the oil and recovering a non-crystalline part.

The crude palm oil to be used in the present invention is an oil obtained from fruits of oil palms as it is. Oil palms are palm trees and their variety is not specifically limited but examples thereof include the Dura species, Tenera species and Pisifera species. The crude palm oil contains 500 ppm to 3,000 ppm of carotene and up to about 90% thereof are α-carotene and β-carotene.

The crude palm oil thus obtained is completely dissolved in an organic solvent for example by warming. Examples of the organic solvent include ethanol, acetone, Hexane and a mixtures thereof.

The concentration of the crude palm oil in the solution is 5 to 30% by weight, preferably 10 to 20% by weight. When the concentration is less than 5% by weight, a facility for producing the carotene concentrated oil and recovery of the solvent becomes expensive. On the other hand, when the concentration exceeds 30% by weight, fractionation by cooling cannot be carried out and recovery of carotene is significantly lowered.

The cooling operation itself is not specifically limited. However, the cooling rate should be 1°C or less per minute, preferably 0.8°C or less per minute, more preferably 0.8°C to 0.3°C per minute. When the cooling rate exceeds 1°C per minute the rate of precipitation of fine crystals becomes too fast and carotene is incorporated into the fine crystals, which makes recovery of carotene difficult.

The precipitation of fine crystals is also influenced by the stirring rate of the solution. However, the stirring rate is selected according to the oil content of the solution and therefore the stirring rate is not limited in the present invention.

The end point temperature of cooling is selected according to the solvent and the concentration of the dissolved oil. For example, when hexane is used as the solvent and the solution is cooled to -20°C, 98% or more of carotene can be recovered.

Recovery of the non-crystalline part can be carried out by a conventional method. For example, after separation of solids (crystals) from a liquid fraction by suction filtration, the recovered crystals on the filter are washed with the solvent used and the filtrate is combined with the liquid fraction. Since the recovered non-crystalline part contains the solvent, the solvent is removed by a conventional method such as distillation.

Although the carotene content of the carotene concentrated oil thus obtained varies according to the particular crude palm oil used, normally the carotene concentrated oil contains about 2 to 4 times more carotene than the starting oil, i.e., a carotene concentration of 1,000 to 15,000 ppm.

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof. In the Examples and Comparative Examples, all "ppm's", "parts" and "percents" are by weight unless otherwise stated.

Example 1

Crude palm oil (15 parts, carotene concentration: 853 ppm) was dissolved in hexane (85 parts) warmed to 40°C and the solution was cooled to -20°C at a cooling rate of 0.5°C/min. with stirring at 60 r.p.m. Thereafter, solids were separated from the liquid fraction by suction filtration and the resulting crystallin part was washed with hexane (30 parts) at -20°C to recover a non-crystalline part.

Hexane from the non-crystalline part was remov d by distillation and then activated clay was added in an amount of 1% based on the weight of the oil. Bleaching was carried out at 100°C under a reduced pressur of 5 Torr and steam was blown through at 140°C for 180 minutes under a reduced pressure of 2 Torr to obtain a

carotene concentrated oil. The carotene concentrated oil contained 2,250 ppm of carotene and was tasteless and odorless.

By using this carotene concentrated oil, an emulsion drink was prepared according to the formulation as shown in Table 1 and its flavor was organoleptically evaluated by 10 panelists.

Table 1

| Formulation of emulsion | |
|---|---|
| Ingredient | Amount (%) |
| Carotene concentrated oil | 6.0 |
| Skimmed milk powder | 10.0 |
| Refined sugar | 1.0 |
| Lecithin | 0.03 |
| Carrageenan | 0.5 |
| Sodium hydrogen phosphate | 0.05 |
| Sodium polyphosphate | 0.25 |
| Salt | 0.03 |
| Water | up to 100 |

Comparative Example 1

Commercially available palm carotene was added to refined super-palm olein in a concentration of 2,250 ppm to obtain a carotene concentrated oil. By using this carotene concentrated oil and according to the same method as described in Example 1, an emulsion drink was prepared and its flavor was organoleptically evaluated by 10 panelists.

As shown in Table 2, the carotene concentrated oil produced by the process of the present invention (Example 1) is tasteless and odorless and, when it is used in a drink, clearly it does not diminish the flavor or taste of the drink.

Table 2

| Flavor evaluation panel test | | |
|---|---|---|
| | Flavor of carotene concentrated oil | Flavor of drink (number of persons who felt it palatable) |
| Example 1 | tasteless oderless | 9 |
| Comparative Example 1 | solvent odor | 1 |

Example 2

Refined palm oil (70 parts) was mixed with refined coconut oil (30 parts). To the mixture was added commercially available palm carotene 30% concentrate so that the final concentration of carotene became 5,000 ppm. Steam was blown through at a deodorizing temperature of 120°C for 60 minutes under a reduced pressure of 1 Torr to obtain a carotene concentrated oil containing 4,958 ppm of carotene. By using this carotene concentrated oil, ice cream was prepared according to the formulation as shown in Table 3 and its flavor was organoleptically evaluated by 10 panelists.

Comparative Example 2

According to the same method as described in Example 2, ice cream was prepared and its flavor was organoleptically evaluated by 10 panelists except that the carotene concentrated oil prepared by addition of the commercially acceptable palm carotene 30% concentrate in a concentration of 5,000 ppm was not subjected to the deodorization step.

As shown in Table 4, when a frozen confection such as ice cream is prepared by using the carotene concentrated oil of the present invention (Example 2), the oil does not diminish the flavor of the food material.

Table 3

| Formulation of ice cream | |
|---|---|
| Ingredient | Amount (%) |
| Carotene concentrated oil | 10.0 |
| Skimmed milk powder | 5.6 |
| Refined sugar | 1.3 |
| Thick malt syrup | 10.0 |
| Condensed milk | 18.5 |
| Butter | 2.0 |
| Water | up to 100 |

Table 4

| Flavor evaluation panel test | | |
|---|---|---|
| | Flavor of carotene concentrated oil | Flavor of drink (number of persons who felt it palatable) |
| Example 2 | tasteless odorless | 10 |
| Comparative Example 2 | solvent odor | 0 |

Example 3

Preparation of carotene concentrated oil

Crude palm oil (carotene content: 720 ppm) (450 g) was dissolved in hexane (2,550 g) at 60°C so that the oil content became 60% and the solution was cooled to -20°C at the cooling rate of 0.5°C/min. After cooling, the crystalline part was removed by suction filtration and then hexane was removed to obtain a carotene concentrated oil (244 g, carotene content: 1,326 ppm). This carotene content corresponded to about 1.84 times the concentration of the carotene content of the starting oil and recovery of carotene was about 99.9%.

Comparative Example 3

Preparation of carotene concentrated oil

According to the same method as described in Example 3, a carotene concentrated oil was prepared except that the cooling rate was 5°C/min. As a result, although a carotene concentrated oil (215 g, carotene content: 760 ppm), only about 1.06 times the carotene concentration of the starting oil was obtained. Recovery of carotene was about 50.4%. Thus, when the cooling rate was faster, the concentration of carotene was reduced and recovery of carotene was reduced. This became impractical.

As described hereinabove, according to the present invention, a high carotene content oil which is cheap and has a palatable flavor can be obtained. Therefore, the high carotene content oil can be generally used in the production of foods.

## Claims

1. A process for producing a high carotene content oil which comprises blowing steam through an oil containing carotene in an amount of at least 500 ppm under a reduced pressure of not higher than 10 Torr whilst maintaining the temperature at 110 to 150°C.

2. A process as claimed in claim 1, wherein the oil through which steam is blown contains 500 to 30,000 ppm of carotene.

3. A process as claimed in claim 1 or claim 2, wherein the oil through which steam is blown is an oil obtained by dissolving crude palm oil in an organic solvent at a concentration of 5 to 30% by weight, the process further comprising cooling the resulting solution at a cooling rate of, at the highest, 1°C/min. to precipitate a crystalline part of the oil and recovering a non-crystalline part.

4. A process as claimed in any preceding claim wherein the steam blowing is carried out for 30 to 200 minutes when 3.3% by weight of steam based on the oil is blown per hour.

5. A process as claimed in any preceding claim wherein the high carotene content oil produced contains 500 to 30,000 ppm of carotene.

6. Use of a high carotene content oil when produced by a process as claimed in any preceding claim in, or as, a food.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 95 30 1329

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| P,X | WO-A-94 12596 (UNILEVER)<br>* page 2, line 10 - page 3, line 18 *<br>* page 4, line 10 - line 35 *<br>* page 5, line 9 - page 6, line 1 *<br>* claims 1-3,7-14 * | 1,6 | C11B3/14<br>C11B7/00<br>A23D9/00 |
| Y | AU-B-632 272 (PALM OIL RESEARCH INSTITUTE OF MALAYSIA)<br>* the whole document * | 1-6 | |
| Y | DATABASE WPI<br>Week 7730<br>Derwent Publications Ltd., London, GB;<br>AN 77-53198Y<br>& JP-A-52 071 509 (ASAHI DENKA KOGYO) , 15 June 1977<br>* abstract * | 1-6 | |
| A | GB-A-2 141 438 (INSTITIUT PENYELIDIKAN MINYAK KELAPA SAWIT MALAYSIA)<br>* page 1, line 21 - line 28 * | 1-6 | |
| A | DE-A-38 39 017 (HENKEL)<br>* page 2, line 49 - line 57 *<br>* claims 1,4-7 * | 1 | TECHNICAL FIELDS SEARCHED (Int.Cl.6)<br>C11B<br>A23D |
| A | EP-A-0 529 107 (DEUTSCHE GESELLSCHAFT FÜR TECHNISCHE ZUSAMMENARBEIT (GTZ))<br>* abstract * | 1 | |
| A | DATABASE WPI<br>Week 9343<br>Derwent Publications Ltd., London, GB;<br>AN 93-339910<br>& JP-A-05 247 364 (HASEGAWA CO LTD) , 24 September 1993<br>* abstract * | 6 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 31 May 1995 | Dekeirel, M |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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